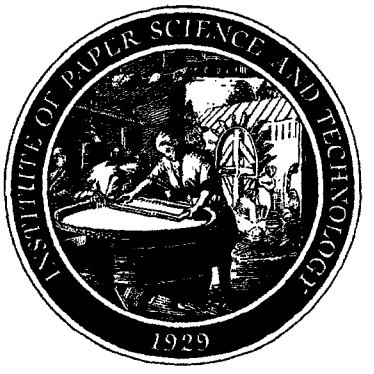

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Applications of Headspace Gas Chromatography in the Pulp and Paper Industry

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Applications of Headspace Gas Chromatography in the Pulp and Paper Industry

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ABSTRACT

Several headspace gas chromatographic (HSGC) methods for the determinations of species concentration and solute vapor-liquid equilibrium partitioning coefficient are presented. The presentation is focused on the applications of these methods to systems with complex matrices, such as streams from pulp and paper mills. The basic operation principles along with the proper operating conditions and procedures of HSGC are provided for practical applications. The HSGC methods are accurate, rapid, and simple in solving complex problems in the pulp and paper industry. The methods can also be used in various other industrial and environmental applications.

INTRODUCTION

Headspace gas chromatography (HSGC) is a powerful technique that has been applied in the food processing, medical, and chemical industries. It relies on the vapor liquid equilibrium of a volatile species in a nonvolatile matrix within a closed container (a sample vial). The volume of the space unoccupied by the nonvolatile matrix is called the headspace (vapor or gas phase space). The basic principle of HSGC and many useful methods can be found in textbooks [1-3] and review articles [4, 5]. Because direct liquid phase probing is not necessary, HSGC eliminates the sample matrix effect on measurements and therefore suitable for industry applications with complex sample matrices. With the advances in chromatographic technology, many commercial HSGC systems are available, making HSGC in industrial applications convenient and practical.

In the pulp and paper industry, the analyses of various volatile and nonvolatile species in complex sample matrices are common practices for product quality control, environmental emission prediction, and process performance monitoring. Although many standard analytical techniques and procedures have been developed by the pulp and paper industry [6], analyses using these standard methods often require complicated and time-consuming analytical procedures because most of the techniques were developed many decades ago before advanced technologies were available. Many practical needs are not met by the standard analytical procedures. On the other hand, the pulp and paper industry, as a traditional industry, is relatively reluctant to accept new analytical techniques that are just being developed.

The present authors have devoted much of their research effort for several years to develop simple, accurate, and practical analytical procedures using advanced commercial instruments for industry applications. In this monograph, we present part of our research effort on the application of headspace gas chromatography for practical needs in chemical analysis and determination of vapor-liquid equilibrium (VLE) in the pulp and paper industry. These procedures, however, are not limited to pulp and paper industrial applications and can be applied to other industries.

HEADSPACE OPERATING PRINCIPLE

All our research was conducted using a commercial HSGC, i.e., HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA). The basic operating principle is similar to most commercial HSGC systems. Figure 1 shows a schematic diagram of an HP Headspace Sampler. The operation of the sampler is simple. A sample is first placed in a vial, which is then sealed by a septum, and placed in the sample vial tray of the headspace sampler. The unfilled space in the vial is called the headspace. The sample vial is then transported to an oven (a well-controlled temperature environment) and for an equilibrium period to achieve vapor-liquid phase equilibrium. When valve S1 is open and S2 is closed and positions 4 and 5, and 1 and 6 of the injection valve are connected, the sample vial is pressurized by a gas (helium, nitrogen, or air) through a hypodermic needle to create a pressure head for sampling. The vapor phase in the headspace to be analyzed is transferred into the sample loop when valve S1 is closed and S2 is open. The vapor in the sample loop is then injected into the GC column by a carrier gas flow when the positions of 1 and 2, and 3 and 4 of the injection valve are connected. If multiple headspace extraction (MHE) operation is desirable, the procedures described above are repeated on the sample vial. The entire operation is controlled by a personal computer and is fully automated.

HEADSPACE OPERATING CONDITIONS

It is important to operate the headspace at a proper set of conditions for accurate measurements. Most of the HSGC techniques rely on the VLE of the analyte in the headspace. Therefore, it is critical to achieve analyte equilibrium in the vial static headspace. We conducted the equilibrium test at 70°C using an aqueous methanol solution to obtain the desired vial equilibrium time through HSGC analysis of the headspace vapor. As shown in Fig. 2, the signal peak area of the GC flame

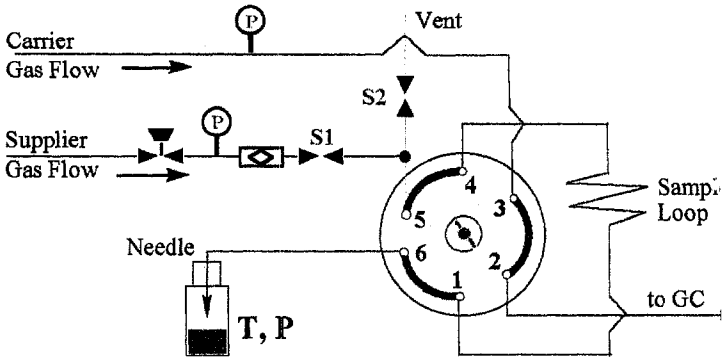

Fig. 1. A schematic diagram of a headspace injection system.

ionization detector (FID) increases with equilibrium time and then reaches a constant value, indicating that VLE of methanol has been established. Figure 2 also shows that a large sample size requires a longer equilibrium time as expected. Figure 3 shows the effect of sample size on equilibrium time for an aqueous methanol solution. Although the equilibrium time also varies with the sample matrix, the data presented in Fig. 3 can be used as a guideline for methanol analysis in kraft mill streams.

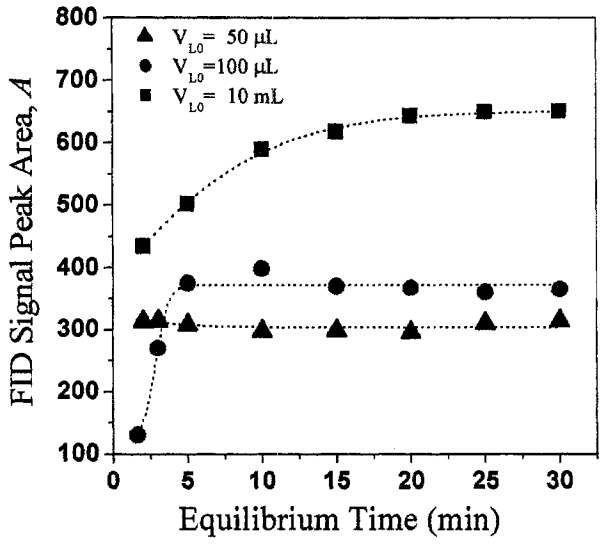

Fig. 2. The effect of vial equilibrium time on measured GC FID signal peak area.

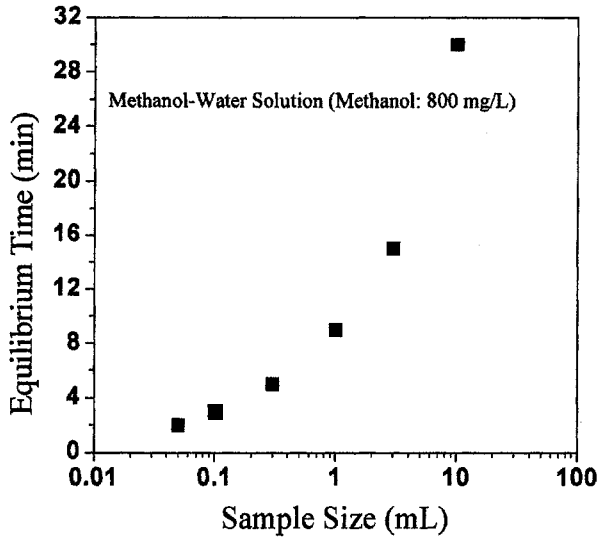

Fig. 3. The effect of sample size on vial equilibrium time.

Vial pressurization is used in most commercial headspace samplers to create a pressure head within the vial for sampling. Vial pressurization reduces the analyte concentration in the headspace, raising the issue of analyte dilution, which will be discussed in the next paragraph. Different headspace samplers may use different control techniques for pressurization. Pressurization time is used for pressurization control with a constant pressure head in the HP-7694 sampler. We tested the effect of vial pressurization time on measured GC FID signal peak area using an aqueous methanol solution. Because pressurization dilutes the analyte concentration within the headspace, the measured signal decreases with pressurization time initially as shown in Fig. 4 and then reaches a constant level because a fixed pressure head is used. Although pressurization time can affect GC signal, it should not affect the accuracy of absolute measurements through calibration as long as the same pressurization time is used for both the calibration and testing experiments. Several HSGC techniques use the ratio, r_A, of the GC signal peak areas obtained from two separate measurements using two different sample sizes. We plotted r_A in Fig. 4 and found that r_A is not affected by the vial pressurization time. A pressurization time of 0.2 min is used in most of our experiments.

The sample-loop in most commercial headspace samplers is filled through venting the pressurized vial to atmosphere. The venting time is used to control the sample-loop filling process. W studied the effect of sample-loop fill time on measured FID signal peak area using a methanol-water solution. As shown in Fig. 5, the measured FID signal peak area reaches a constant level at about a loop fill time of 0.2 min for the two sample sizes tested. A constant ratio of the two signals is also achieved with a loop fill time of 0.2 min. A longer loop fill time, e.g., 0.2 min, can also lead to an atmosphere pressure within the sample vial, important in multiple headspace extraction (MHE) HSGC measurements.

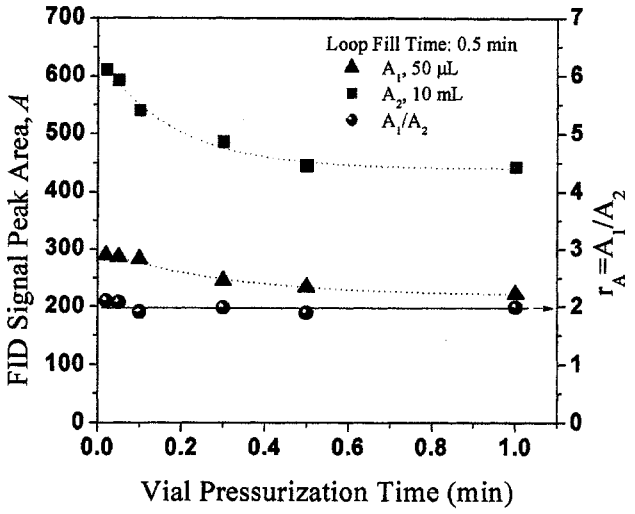

Fig. 4. The effect of vial pressurization time on measured FID signal peak area.

QUANTITATIVE ANALYSIS

The difficulties in species analysis in the pulp and paper industry occur mainly because samples from the streams of pulp and paper mills often have complex matrices. A typical example is spent pulping liquor, which is called black liquor because of its color. Black liquor contains dissolved organic solids such as lignin, hemicellulose, organic and inorganic salts, hydroxide, and sulfide. Black liquor also contains many volatile organic compounds (VOCs) that were formed during the pulping process. Although the concentrations of these species are low or on the order of a thousand

ppm (mg/L), quantitative analysis of these minor volatile species is of great interest because of environmental concerns about air emission and water discharge. In other applications, the analysis of some major species contained in black liquors is also very important and difficult. For example, the determination of carbonate is critical to the understanding of scaling problems in black liquor evaporators and concentrators, a serious concern in industry practice.

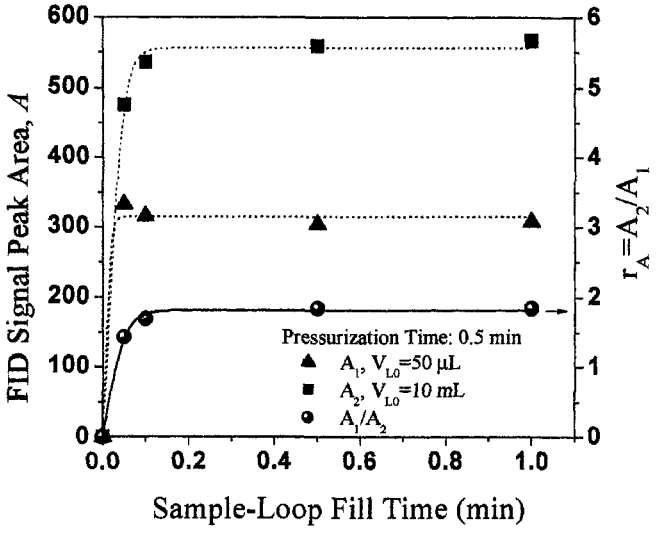

Fig. 5. The effect of sample-loop fill time on measured FID signal peak area.

In the following presentation, we will mainly discuss the application of HSGC for the analysis of methanol, methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and carbonate in black liquors.

The Standard Addition Technique

The standard addition HSGC technique was initially developed by Drozd and Novak [7]. It is based on the thermodynamic VLE and mass balance of the analyte. In a previous study [8], we demonstrated that the method is effective for volatile species analysis in kraft mill streams, including in black liquor.

Figure 6 schematically describes the standard addition method. Two sample vials both filled with the same volume of sample solution were used. A known very small amount of concentrated analyte solution was then added to one of the vials. The volume of the solution added is very small compared to the volume of the original solution and, therefore, can be ignored. After phase equilibrium was established within each vial, headspace GC analysis of each sample was conducted. It can be assumed that the analyte concentrations in these two sample vials are very low or the analyte is under infinite dilution (which is valid for most VOCs in pulp and paper mill streams even after the standard addition). Therefore, the analyte VLE partitioning in these two vials follows Henry's law, which connects the two independent headspace measurements as shown. Together with the material balance equation of the analyte, the following mathematical expression of the analyte concentration in the original sample can be obtained [7, 8]:

$$C_0 = \frac{C_S V_S}{(C_{G2}/C_{G1} - 1)\cdot V_{L0}} \qquad (1)$$

C_0 is the concentration of the analyte to be determined, V_{L0} is the initial sample volume in the testing vial, and V_S and C_S are the volume and analyte concentration of the solution used for spiking (added to the testing vial) through the standard addition. C_{G2}/C_{G1} is the ratio of the analyte vapor phase concentrations in the headspace of the two vials that is proportional to the ratio r_A of the GC signal peak areas A_2 and A_1 of the two HSGC measurements. We can rewrite Eq. (1) as,

$$C_0 = \frac{C_S V_S}{(A_2/A_1 - 1)\cdot V_{L0}} = \frac{C_S V_S}{(r_A - 1)\cdot V_{L0}} \qquad (2)$$

Calibration is not needed with Eq. (2) for VOC analysis. We validated Eq. (2) through the measurements of standard methanol, acetone, and methyl ethyl ketone (MEK)- water solutions in a known concentration range of 0-2000 mg/L. Excellent agreement between the measured and the known analyte concentration was obtained [8].

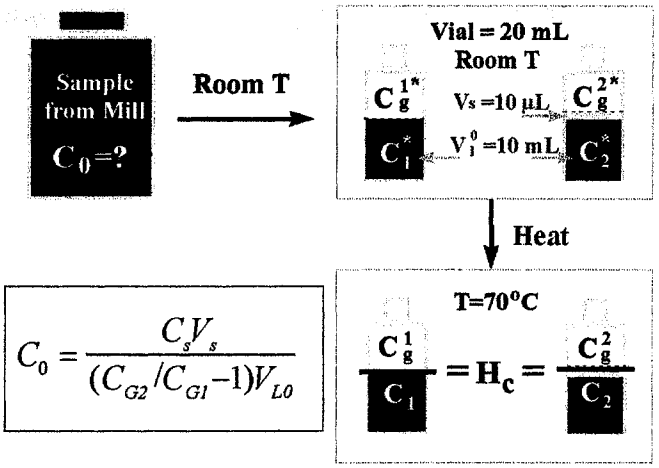

Fig. 6. Schematic diagram describing the indirect HSGC method for analysis of VOCs.

To apply Eq. (2) to analysis of VOCs in various pulp and paper mill streams, especially in black liquors, we first demonstrated that species separation can be achieved with a selected column (HP-5, Hewlett-Packard). Figure 7 shows a typical chromatogram obtained from HSGC analysis of a softwood kraft black liquor sample. Black liquor contains many volatile and low volatile species, as can be seen. In this particular application, we are mainly interested in analyzing the concentrations of methanol and MEK. Although peaks of DMS and DMDS were separated very well, their analysis is much more complicated and will be discussed in the next section.

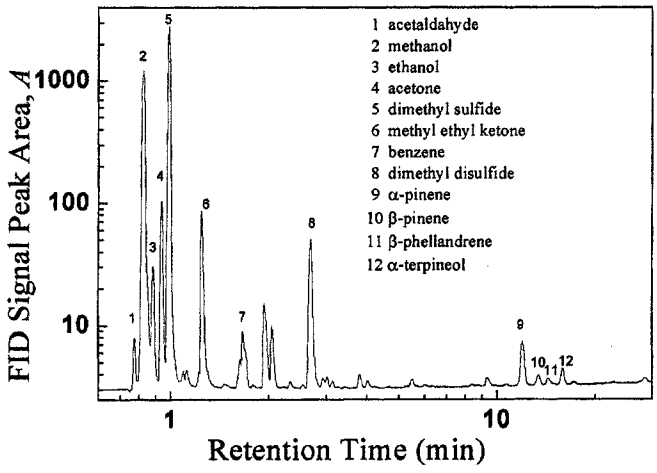

Fig. 7. A typical chromatogram of a softwood kraft black liquor vapor obtained from HSGC analysis with FID.

We have successfully applied the standard addition HSGC method to study methanol formation during alkaline pulping [9] through the analysis of methanol concentration in the spent pulping liquors.

The Full Evaporation Technique

The full evaporation (FE) technique was initially developed by Markelov and Guzowski [10]. It uses a very small sample size to achieve a near-complete transfer of analytes from a condensed matrix into a vapor phase in a very short period of time; therefore, it does not require sample pretreatment. It should be pointed out that complete evaporation of the condensed analyte is not necessary [10]; only a near-complete transfer of the analyte into the vapor phase is required.

Analysis of organic sulfur compounds, e.g., MM, DMS, and DMDS, in black liquor is a difficult task. The tedious and time-consuming solvent extraction technique [11, 12] is most commonly used. With some of the high extraction efficiency solvents, e.g., carbon tetrachloride, being prohibited in many countries due to environmental regulations, the FE HSGC method provides a technically superior and environmentally sound alternative to the solvent extraction method reported some 30 years ago [11, 12]. Because near-complete evaporation is achieved, a gas standard can be used to calibrate HSGC measurements—a key advantage for the analysis of MM since a liquid standard of MM cannot be obtained in an ambient environment.

Detailed mathematical derivation of the FE HSGC method can be found in the work of Markelov and Guzowski [10]. A material balance of an analyte dispensed into a sampling vial can be described by the following equation after thermal equilibrium of the sample:

$$C_G = M_0/(KV_R + V_G) \qquad (3)$$

where C_G is the equilibrium concentration of the analyte in the vapor phase (headspace), M_0 is the initial mass of the analyte in the sample, and K =

C_L/C_G is the analyte phase partition coefficient. V_R is the sample residual volume after thermal equilibrium (the volume of the condensed phase may change significantly after thermal equilibrium due to heating), and V_G is the volume of the vapor phase (headspace).

In the case of near-complete evaporation, the term of KV_R in Eq. (3) is significantly smaller than the headspace volume V_G, i.e., $KV_R << V_G$, and, hence,

$$C_G \approx M_0/V_G. \quad (4)$$

Therefore, the effect of K (a sample matrix-dependent parameter) is eliminated.

Special procedures are required to analyze MM in kraft black liquor. Most of the MM is present in the form of mercaptide ion in black liquor due to the alkalinity of the liquor. Acidification of the liquor is required to obtain total MM measurement. Furthermore, MM can be easily oxidized when in contact with air; therefore, a purge of the sample vial with nitrogen is necessary. Fresh black liquor is collected and dispensed into a sampling bottle that has been thoroughly purged with nitrogen. No headspace is left in the sample bottle. The bottle is then air-sealed and stored in a refrigerator. When analysis is needed, 10 μL of black liquor is dispensed into a sample-testing vial, by a syringe. The testing vial is also thoroughly purged with nitrogen and sealed before the sample is added. For a sample vial of 20 mL, a 2-min nitrogen purge at a flow rate of 130 mL/min is sufficient to eliminate the effect of oxidation of MM by oxygen in air [13]. 50 μL of 0.5-mol/L sulfuric acid then is added to the testing vial to acidify the black liquor for total MM measurement.

We used a pulsed flame photometric detector (PFPD) made by O.I. Analytical, (College Station, TX, USA) for sulfur compound analysis in black liquors. The selectivity of sulfur to hydrocarbon of the PFPD is 10^5:1, very suitable for the analysis of sulfur compounds in black liquor that contains many other VOCs. By observing the square root of the DMS signal peak area of PFPD while varying the sample size, we found that near-complete evaporation can be achieved with a sample size as large as 400 μL in analysis of kraft black liquor at a headspace sampler temperature of 80°C [13]. Because near-complete evaporation is achieved, quantitative analysis can be performed through calibration using both gas and liquid standards based on the following expression [13, 14]:

$$m = k\sqrt{A} \quad (5)$$

Because PFPD has a very high selectivity of sulfur to hydrocarbon, most of the volatile hydrocarbon species can be effectively eliminated from the chromatogram. Figure 8 shows a typical chromatogram obtained from FE HSGC analysis of an acidified kraft black liquor sample using a PFPD. The signal peaks of MM, DMS, and DMDS are well separated. The strong saturated peak is due to the formation of H_2S and SO_2 from sodium sulfide (a major species contained in kraft black liquor) and thiosulfate by acidification.

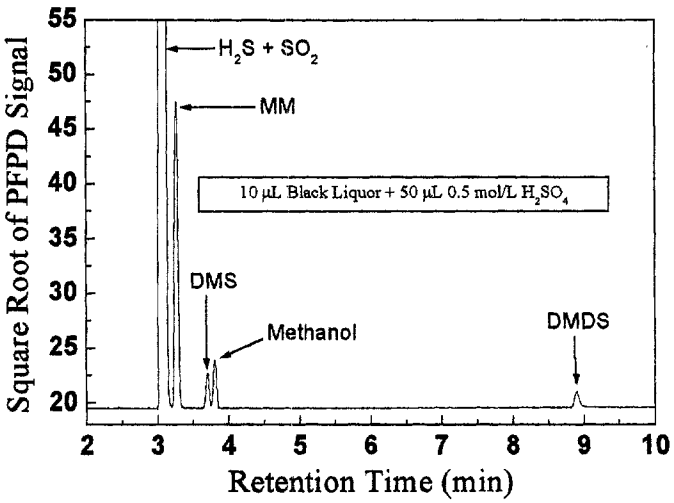

Fig. 8. A typical chromatogram of a kraft black liquor obtained through FE HSGC analysis with PFPD.

We used soda black liquors (obtained from hydroxide pulping) to demonstrate matrix independence in the analysis of black liquor by FE HSGC. The soda liquors were obtained by terminating the soda pulping process at various cooking times so that the solids content and composition are different. The soda liquors should have sample matrices similar to those of kraft

liquors under the same delignification conditions except that soda liquors do not contain any sulfur compounds. A known amount of 1 μg of DMS was added to each soda black liquor with a sample size of 12 μL, and the DMS signal peak area of the PFPD was recorded. We found that the relative standard deviation of the 7 measurements in the soda liquor samples with solids content varying from 1 to 17.6% was only 4.1% [13], indicating that the black liquor sample matrix does not affect the FE HSGC measurements.

The measurement of sulfur compounds in black liquor using Eq. (5) is validated by adding various known amounts of DMS to a soda black liquor with solids content of 15%. Good agreement was obtained between the amounts of DMS measured and those added, as shown in Fig. 9.

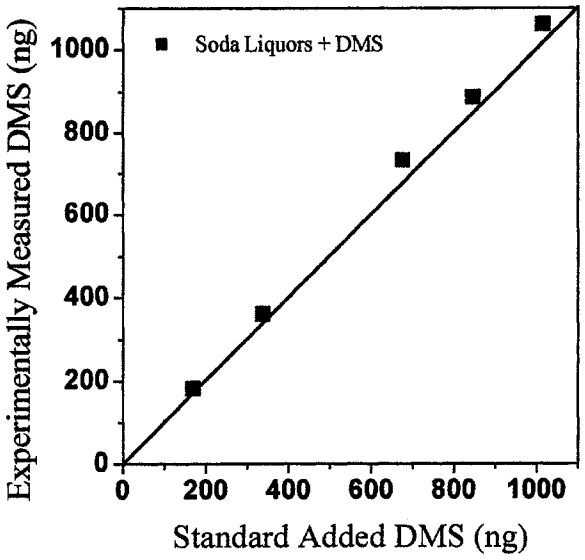

Fig. 9. Comparison of measured DMS in soda liquor samples with the known amounts of DMS spiked prior to measurements.

We applied the FE HSGC method to study the formation of organic sulfur compounds during kraft pulping [15]. We used an integrated approach to investigate the relationship between delignification and sulfur compound formation. From this study we discovered a phase transition point (PTP) below which the formation of total reduced sulfur compounds (TRS) increases significantly. Based on PTP, we proposed an In-Digester Odor Reduction (IDOR) methodology for further TRS reduction in kraft mills.

A Chemical Reaction Technique for Nonvolatile Species Analysis

Most of the HSGC techniques, including the two described above, are suitable for the analysis of volatile species and cannot be applied to nonvolatile species. To take advantage of the matrix-independent HSGC analysis, we developed a chemical reaction (CR) technique [16] for some nonvolatile species analysis. Specifically, we developed a CR HSGC procedure to analyze carbonate content in black liquor. This analysis is valuable in preventing scaling in weak black liquor concentrators or evaporators, a severe problem that affects pulp and paper production. However, such an analysis is difficult due to the complex sample matrix of black liquor. Titrametry has failed because of the presence of organic salts. The application of capillary ion electrophoresis [17] and ion chromatography [18-20] for carbonate analysis in black liquors requires complicated sample pretreatment. The sensitivity and repeatability of the measurements are poor. The time-consuming coulometric technique [21], though used in commercial analytical laboratories for carbonate analysis in black liquors, presents difficulties and measurement uncertainties due to the interference of other volatile species released during liquor acidification.

CR HSGC is based on a common practice in analytical chemistry, i.e., conversion of a fixed percentage, including complete conversion, of an unknown nonvolatile analyte in a liquid sample into gas products through chemical reactions. The analyte is then analyzed through the measurements of the gas products using HSGC. As long as the conversion rate is a constant, quantitative analysis of the nonvolatile analyte in a sample can be achieved through calibration. We have derived the following expression, (shown in Eq. (6)) for the calculation of analyte concentration in an unknown sample based on a one-step conversion reaction shown in reaction (7),

$$C_B = \frac{1}{\alpha}\cdot\frac{b}{q}\cdot\frac{V_T - V_L}{V_S}\cdot C_Q \qquad (6)$$

$$rR + bB(liquid) \longleftrightarrow pP + qQ(gas) \qquad (7)$$

where C_B and C_Q are the molar concentrations of the analyte B in the original sample solution to be determined. α is the reaction conversion rate of analyte B. b and q are the stoichiometric coefficients in reaction (7). V_T and V_L are the volumes of the reactor (sample vial) and the postreaction residual liquid, respectively, and V_T-V_L is the postreaction headspace volume. V_s is the initial volume of the unknown sample used in measurement. C_Q is the molar concentration of the product gas Q in the headspace at the complete of the reaction. When the initial sample volume is very small, i.e., $V_s < 5\%\cdot V_T$ (1 mL for V_T = 21.6-mL vial), the postreaction headspace volume can be approximated to the volume of the sample vial, i.e., V_T-$V_L \approx V_T$. Because C_Q is proportional to the GC detector signal peak area, i.e., $C_Q = k'A$, and α is a constant for a given experiment, Eq. (6) can be rewritten as,

$$m_B = kA \qquad (8)$$

where k is a calibration constant.

To apply Eq. (8) for carbonate analysis in black liquor, we used sulfuric acid as reactant R to convert carbonate to carbon dioxide (CO_2) according to the following reaction:

$$2H^+ + CO_3^{2-} \Rightarrow CO_2 + H_2O \qquad (9)$$

an overdose of sulfuric acid is used due to the alkalinity of black liquor, i.e., V_R = 0.5 mL of 2 mol/L sulfuric acid is used to acidify a sample containing less than 200 μmol of carbonate. A thermal conductivity detector (TCD) is used to measure CO_2 concentration in the headspace gas after acidification.

Because CO_2 concentration in air is about 15 μmol/L, there are about 0.3 μmol of CO_2 present in the 21.6-mL vial, greater than the sensitivity of the TCD of 0.1 μmol. A nitrogen purge of the sample vials is necessary to eliminate the effect of CO_2 in air on measurement accuracy.

To demonstrate that analyte dilution due to vial pressurization has negligible effect on measurement accuracy, we conducted HSGC measurements in 9 aqueous carbonate samples that contained the same amount of carbonate of 1.06 μg. The sample volumes, V_s, varied from 100 to 350 μL. We found that the relative standard deviations of the 9 measurements is only 1.3%, indicating that there is a negligible effect of variations in headspace dilution induced by the variations in initial total volume of the two reactants (V_R+V_S) from 600 to 850 μL.

The constant conversion rate of the nonvolatile species (carbonate) was verified through two sets of experiments using an aqueous 0.1 mol/L sodium carbonate solution and a kraft black liquor, respectively. The sample size was varied in each set of experiment. It was found that the TCD signal peak area varies linearly with sample size, indicating that the conversion of carbonate to carbon dioxide is a constant. Figure 10 shows the results obtained using the black liquor. The results again indicate that headspace dilution induced by sample size (within the tested range) does not affect measurement.

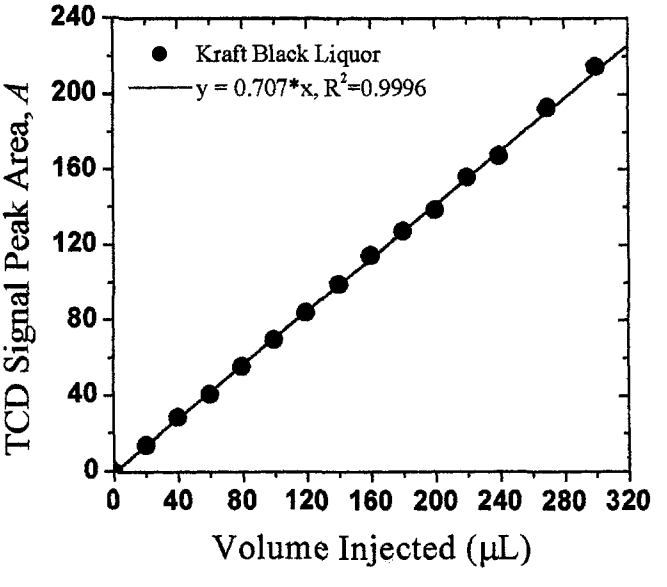

Fig. 10. Verification of constant rate of conversion of nonvolatile species under different sample sizes.

Measurement precision was tested using both the aqueous carbonate solution and a kraft black liquor. Replicas of the CR HSGC experiment were conducted using five samples of equal volume of 100 μL. The relative standard deviations of the measured TCD signal peak areas were only 0.025% for the carbonate solution and 0.15% for the black liquor, indicating the precision of the method.

We used the 0.1-mol/L aqueous carbonate solution as an external standard to calibrate carbonate measurements in kraft liquors. We used a standard addition technique to validate the method. We added various known amounts of sodium carbonate to an unknown black liquor sample of 100 μL. CR HSGC measurements indicated that the measured TCD signal peak areas fit to a straight line very well as shown in Fig. 11. The absolute value of the intercept of 4.5 μmol on the x-coordinator of the fitted line is the original carbonate contained in the unknown black liquor sample. Using Eq. (8), we then calculated the carbonate in the sample to be 4.4 μmol. The difference was only 2.2%, indicating the validity of the CR HSGC method for carbonate determination in black liquor.

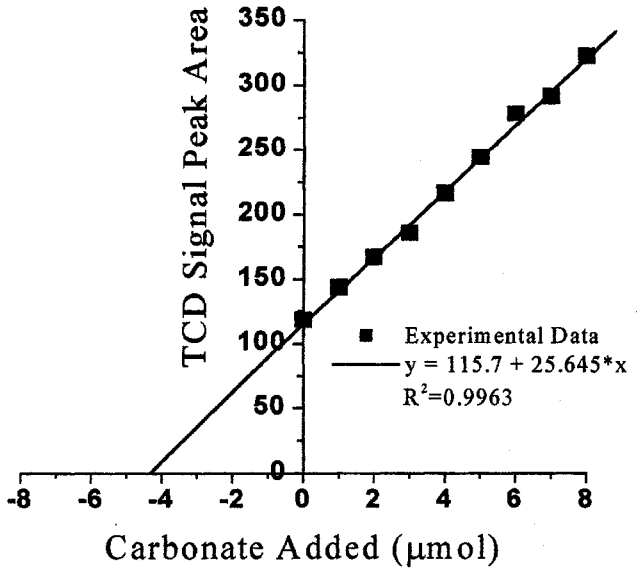

Fig. 11. Validation of measured carbonate in black liquor by a standard addition method.

We applied the CR HSGC method to study carbonate concentration in black liquors collected from various stages of a kraft mill evaporator system. The data provided useful information for early warning of evaporator scaling.

VLE DETERMINATION

The complex sample matrix of many streams from pulp and paper mills also makes VLE determination of solute difficult. In this section, we will discuss three HSGC methods for VLE analysis of methanol in various pulp and paper mill streams. Because the concentrations of methanol and many other VOCs in mill streams are low and can be treated under infinite dilution, determination of Henry's law constant is the main objective of VLE analysis.

Henry's law constant is defined according to the following equation:

$$H_i = \lim_{x \to 0} \frac{P_i^v}{x_i} = \lim_{x \to 0} \frac{y_i \cdot P}{x_i} \qquad (10)$$

where x_i and y_i are the mole fraction of the species i in the liquid and vapor phase, respectively. For a system at equilibrium in a static headspace, the vapor phase can be assumed to follow the ideal gas law,

$$y_i \cdot P = P_i^v = C_{Gi} \cdot RT \qquad (11)$$

where C_{Gi} is the solute mole concentration in the headspace (vapor phase) and R is the universal gas constant. In a system in which all solutes are at infinite dilution, the mole fraction of solute i in the liquid phase can be approximated as

$$x_i \approx \frac{n_i}{n_j} = \frac{C_{Li}}{\rho_j / M_j} = C_{Li} \cdot v_j \qquad (12)$$

where C_{Li} is the solute concentration in the liquid phase at equilibrium, and ρ_j, M_j, and v_j are the density, molecular weight, and the molar volume of the solvent, respectively. Equation (12) is still a good approximation even for spent pulping liquors with total solids content around 20%.

Combining Eqs. (11), (12), and (10) leads to a relationship between the Henry's constant of species i and its partition coefficient $K_i = C_{Li}/C_{Gi}$ in a static headspace:

$$H_i = \frac{RT}{v_j K_i} = \frac{\rho_j RT}{M_j \cdot K_i} \tag{13}$$

The Direct Method

The direct HSGC method for VLE analysis was demonstrated by Kolb et al. [22]. It simply measures the equilibrium solute concentrations in the liquid and vapor phase separately and directly for the calculation of K_i and H_i. With headspace measurement, the equilibrium solute concentration in the vapor phase can be easily expressed in terms of the measured GC detector peak area A, i.e.,

$$C_{Gi} = f \cdot A \tag{14}$$

Because the equilibrium solute concentration in the liquid phase can be calculated from the initial solute concentration in the original sample based on material balance, we have,

$$K_i = \frac{C_{Li}}{C_{Gi}} = \frac{C_0 - \beta C_{Gi}}{f \cdot A_i} \tag{15}$$

where f is the GC response factor and $\beta = V_G/V_L$ is the phase ratio.

Equation (15) is valid for determination of the VLE partitioning coefficient, K_i, in any systems. We applied Eq. (15) to determine Henry's law constant of methanol in black liquors in a previous study [23]. An FID is used. In the study, the volume of the sample vial was 20 mL and the liquor sample size was 10 mL for all the experiments conducted, which gave the headspace volume of 10 mL and the phase ratio $\beta = 1$. Therefore, if K_i is much greater than 1, i.e., $K_i > 10$, $C_{Gi} << C_{Li}$ ($< C_0$) can be ignored in Eq. (15), and, hence,

$$K_i \approx \frac{C_0}{f \cdot A_i} \tag{16}$$

We adopted an external calibration standard to obtain the GC response factor f by using a standard aqueous methanol solution with known methanol concentration of C_{s0} = 800 mg/L and methanol VLE partition coefficient K_{si}, (e.g., K_{si} = 570 at 70°C [24]), and, hence,

$$K_i = \frac{A_{si}}{A_i} \cdot \frac{C_o}{C_{so}} \cdot K_{si} \tag{17}$$

where A_{si} is the FID signal peak area recorded in measuring the headspace vapor of the standard solution at the temperature corresponding to K_{si}.

Equation (17) is especially suitable for VLE analysis in black liquor. We have used Eq. (17) to obtain a semiempirical correlation for the prediction of Henry's constant of methanol in black liquor [23].

The Modified Method of Equilibrium Partitioning in Close Systems (EPICS)

The EPICS method was initially developed by Lincoff and Gossett [25, 26]; it determines Henry's law constant indirectly based on the VLE of the solute in a closed system and on solute mass conservation. In the method, two sample vials were used, and the volume ratio of the two testing solutions was arbitrarily taken as 10 [25] and 4 [26]. The mass of the solute in the two solutions was equal [25], or the mass ratio was measured [26]; therefore, the solute concentrations in the two vials were different. It was assumed that the solute in two solutions was under infinite dilution; therefore, the VLE partitioning coefficients of the solute in these two solutions are equal at a given temperature. The advantages of the EPICS method are that no special apparatus is required and calibration is not necessary. Henry's constant can be obtained by measuring the vapor concentration ratios from a pair of sealed vials with different solution volumes and solute concentrations through headspace gas chromatography.

Later Kolb et al. [27] took a similar approach but conducted several headspace measurements. They used several vials filled with the same solution but with different volumes, instead of using two vials filled with solutions of different solute concentrations. They derived the VLE

partitioning coefficient as a function of the vapor phase concentration, solute concentration in the original sample, and a volume ratio (sample volume over headspace volume) parameter called the phase ratio. They called the method phase ratio variation (PRV).

In principle, the PRV and EPICS method, are not much different. Both are based on solute VLE in static headspace and mass conservation. The main problem of these two methods is that their accuracy is poor in applied to systems with a large partitioning coefficient, for example K>10 as shown by Gosett in his error analysis [26] and K>144 as indicated by Ettre et al. [27].

From a mathematical point of view, it is sufficient and necessary to solve a VLE problem with two and only two equations (two independent measurements). Therefore, it is not necessary to conduct more than two headspace measurements as required in the PRV method [27]. From a physical point of view, the VLE partitioning coefficient K changes with solute concentration except within the range of infinite dilution in which K can be approximated as a constant. Therefore, it is not appropriate to determine K or even Henry's constant on a very strict basis (the concept of infinite dilution is not well-defined physically and mathematically) using two solutions with different concentrations as adopted in the EPICS method [25, 26].

Based on the above reasoning, we propose to conduct two headspace measurements and only two in two vials filled with the same solution but with different sample volume to further develop the EPICS and PRV method [24]. Figure 12 shows the schematic diagram that described our proposed method. Using the material balance of the solute before and after VLE in the vial static headspace, we derived the following expression for the determination of the VLE partitioning coefficient,

$$\frac{1}{K}=\frac{V_L^1\left(1-C_G^1/C_G^2\right)}{C_G^1/C_G^2\left(V_T-V_L^1\right)-V_L^1/V_L^2\left(V_T-V_L^2\right)} \qquad (18)$$

where V and C are volume and solute concentration, respectively. Subscripts *1* and *2* denote vial number, subscript G and L denote gas and liquid phase, and V_T is the vial volume. Because the solute concentration in the gas phase (headspace) is proportional to the FID signal peak area A, Eq. (18) can be rewritten as

$$\frac{1}{K}=\frac{V_l^1(1-r)}{r\left(V_t-V_l^1\right)-x\left(V_t-V_l^2\right)} \qquad (19)$$

where $r = A_1/A_2$, and $x = V_L^1/V_L^2$.

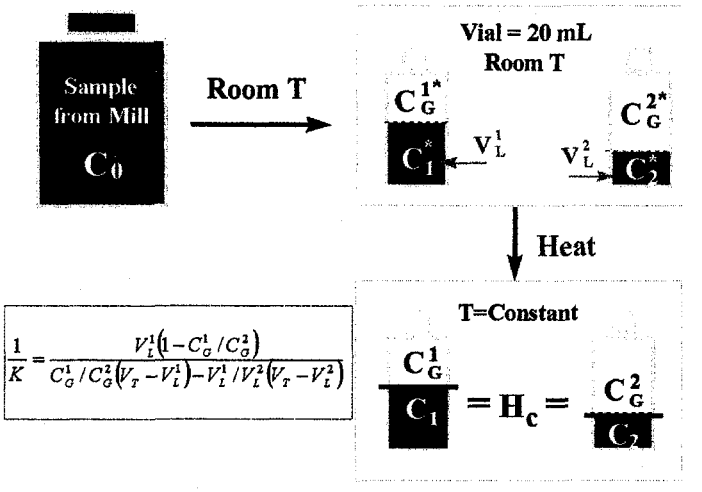

Fig. 12. A schematic diagram that describes the modified EPICS method.

From mathematical analysis, we found that the volume ratio of the two testing samples, x, an independent variable used in the EPICS, PRV, and our proposed method, called the modified EPICS method (M-EPICS), can significantly affect the measurement accuracy. Specifically, we found that accurate measurement of a large partitioning coefficient can be achieved by using a proper x for a given V_L^1. Figure 13 shows the effect of x on the relative variance of partitioning coefficient K with V_L^1=10 mL when the relative error in peak area measurement is 2.5%. The results indicate that the accuracy can be improved in measuring large K by using a large x. When a small sample volume is desired, we also found that accurate measurements can be achieved even with a small x [24].

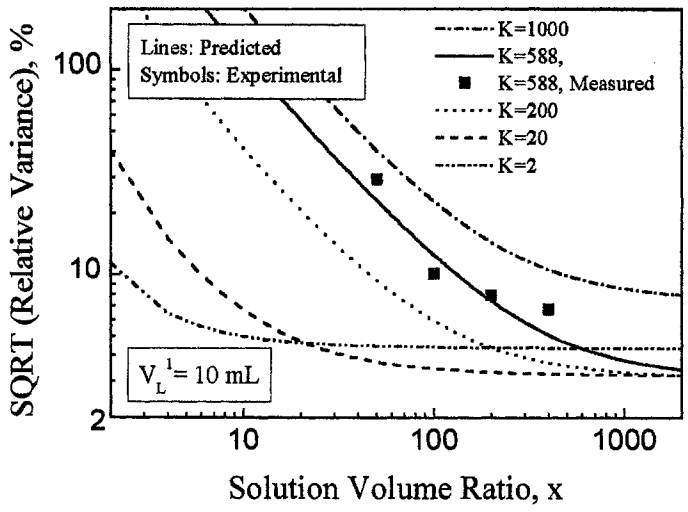

Fig. 13. Effect of sample volume ratio on the accuracy of the refined EPICS method.

The EPICS can only be applied to systems of infinite dilution of solute. However, the M-EPICS can be used to determine solute partitioning coefficient in any systems. We have applied the modified EPICS method to measure Henry's constant of methanol in an aqueous solution. The results agree closely with those reported in the literature [24]. We have also applied the method to determine Henry's constant of methanol in various streams collected in pulp fiber line operation processes so that methanol air emission can be predicted throughout the fiber line.

Multiple Headspace Extraction (MHE) Method

MHE HSGC was developed to achieve analysis automation. It is similar to dynamic gas extraction (or purge-trap), but is carried out in steps. The mathematical model of the MHE method was developed by McAuliffe [28, 29] and Suzuki et al. [30]. The method was further developed by Kolb and Ettre [31-33]. MHE HSGC has been successfully applied in many industries for quantitative analysis [34, 35]. Kolb and Ettre [33, 3] developed an MHE technique for VLE determination; however, they have never demonstrated the technique experimentally. Recently, the present authors developed and experimentally demonstrated an MHE HSGC technique that can simultaneously determine solute concentration and Henry's constant [36]. The method is rapid, automated, and accurate. We also found through experiments that the MHE technique proposed by Kolb and Ettre [33, 3] is inaccurate and produces large uncertainties for VLE determination.

Through mathematical derivation based on solute mass conservation and VLE, we found a key relationship among the MHE-measured GC detector signal peak areas, A_i, [36],

$$\sum_{1}^{n-1} A_i = a + bA_n \qquad (20)$$

where a and b can be determined through linear regression analysis of MHE HSGC-measured GC detector peak areas and are linked to the solute initial concentration, C_o, and VLE partitioning coefficient, K, through the following equations

$$C_0 = f_{MHE} \cdot [a + (b+1)A_n], \qquad (21a)$$

and

$$K = -(1+\varphi b)\beta \qquad (21b)$$

where f_{MHE} and φ are calibration constants, and $\beta = V_G/V_L$ is the phase ratio.

Through mathematical error analysis with the assumption that the square root of the variance of GC peak area is 2.5% of the peak area as well as experimental verification [36], we found that Eq. (21b) is much more accurate than the method of Kolb and Ettre [33, 3]. Figure 14 shows the results of error analysis of the two methods and indicates that the precision of the Chai and Zhu method [36] is at least an order of magnitude better that that of Kolb and Ettre [33,3] in a wide range of Henry's constants.

Good MHE HSGC measurements can be assured by examining the relationship (Eq. (22)) developed by Kolb and Ettre [33] and Eq. (20) using the experimentally obtained GC detector signal peak areas

$$\ln A_i = q \cdot i + p \qquad (22)$$

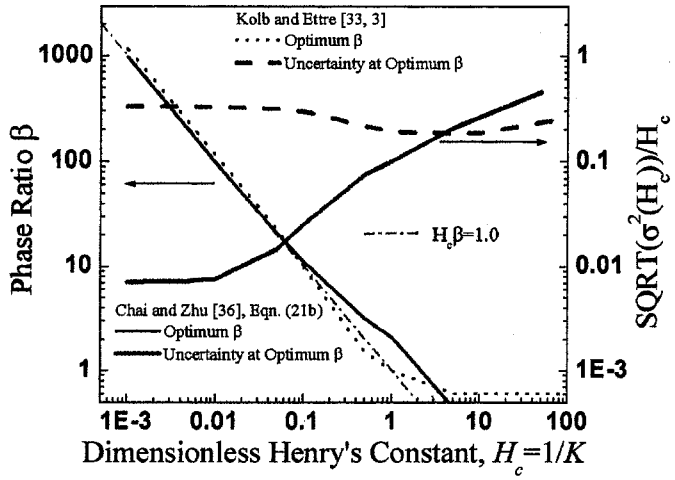

Fig. 14. A comparison of the measurement uncertainties of Henry's constants at the optimum phase ratios between the MHE methods of Kolb and Ettre [33, 3] and Chai and Zhu [36].

Figures 15 and 16 demonstrate these two relationships using one set of MHE HSGC experimental data that we obtained in an aqueous methanol solution [36].

We have successfully applied Eq. (21) for the determination of Henry's constant of methanol in kraft mill streams collected from fiber line operations using Henry's constant of methanol in aqueous solutions for calibration.

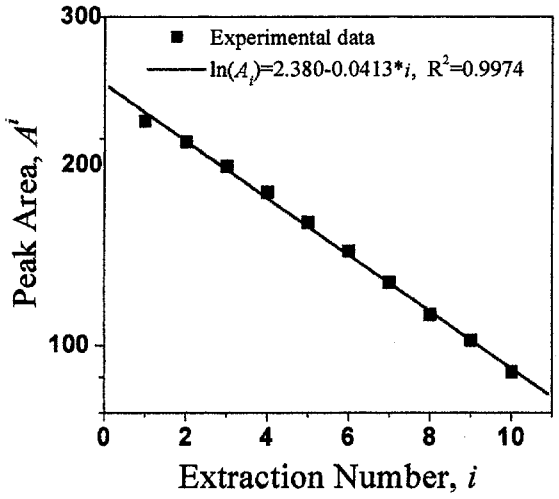

Fig. 15. Experimental verification of Eq. (22)

SUMMARY

This monograph presents and demonstrates several HSGC methods for applications in the pulp and paper industry using a commercial HSGC system. Detailed operating conditions of the system and procedures are provided. It can be concluded that these HSGC methods are accurate, rapid, robust, and simple in solving complex industrial analytical problems. The methods are well suited for various other industrial and environmental applications.

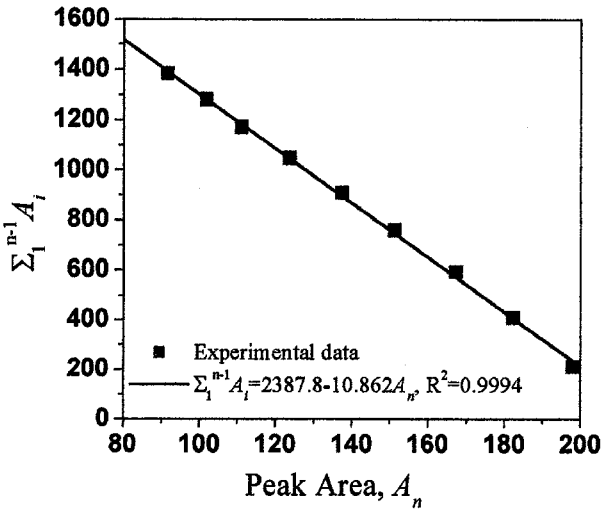

Fig. 16. Experimental verification of Eq. (20)

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